

# PATENT SPECIFICATION

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NO DRAWINGS

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## (54) PERMANENT MAGNETIC PATTERNS

(71) We, A. E. STANLEY MANUFACTURING COMPANY, of Decatur, Illinois, United States of America, a corporation organised under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method of producing permanent magnetic patterns. More particularly, this invention relates to an optical method of producing permanent magnetic patterns.

Magnetic computer tapes and sound tracks have the disadvantage that such tapes are not permanent in the sense that they can be wiped out or erased under the influence of a strong magnetic field. In other cases information is lost due to the sound tape imprinting on itself. Magnetic sound tracks are generally duplicated by audio means, i.e. one or more tapes are replicated by simultaneously playing the audio master and recording the sound track on precoated magnetic tapes. Of necessity, this severely reduces the rate at which tapes can be produced.

The principal object of this invention is to provide a method of producing permanent magnetic tapes. Another object of this invention is to provide an optical method of producing permanent magnetic tapes. Other objects will appear hereinafter.

In the description that follows, the phrase "powder - receptive, solid light - sensitive organic layer" is used to describe an organic layer which is capable of developing a predetermined contrast or reflection density ( $R_d$ ) upon exposure to actinic light and embedment of black powder particles of a predetermined size in a single stratum at the surface of said organic layer. While explained in greater detail below, the  $R_d$

of a light-sensitive layer or  $R_{dp}$  of a positive-acting, light-sensitive layer are photometric measurements of the difference in degree of blackness of undeveloped areas and black powder developed areas. The terms "physically embedded" or "physical force" are used to indicate that the powder particle is subjected to an external force other than, or in addition to, either electrostatic force or gravitational force resulting from dusting or sprinkling powder particles on a substrate. The terms "mechanically embedded" or "mechanical force" are used to indicate that the powder particle is subjected to a manual or machine force, such as lateral to-and-fro or circular rubbing or scrubbing action. The term "embedded" is used to indicate that the powder particle displaces at least a portion of the light-sensitive layer and is held in the depression so created, i.e. at least a portion of each particle is below the surface of the light-sensitive layer.

The objects of this invention can be attained by exposing a non-magnetic base bearing a solid, light-sensitive organic layer of 0.1 to 40 microns thickness and capable of developing a  $R_d$  of 0.2 to 2.2, preferably an  $R_{dp}$  of 0.4 to 2.0, in predetermined areas, corresponding to an optical pattern, to actinic radiation in image-receiving manner to establish a potential  $R_d$  of 0.2 to 2.2; applying to said layer of organic material, free flowing ferromagnetic powder particles, said free flowing powder having a diameter, along at least one axis of at least 0.3 micron but less than 25 times the thickness of said organic layer; while the layer is at a temperature below the melting point of the organic layer, physically embedding said powder particles as a monolayer in a stratum at the surface of said light-sensitive layer to yield an image having portions varying in density in proportion to the exposure of each portion;

removing non-embedded particles from said organic layer to develop a discrete permanent pattern of ferromagnetic material and magnetizing the resultant ferromagnetic material to establish a magnetic pattern corresponding to the original optical pattern.

The invention thus provides an article with a surface having a permanent magnetic pattern comprising a non-magnetic base bearing a solid organic layer of 0.1 to 40 microns thickness, said organic layer comprising the product of an exposed photo-sensitive organic material and containing a monolayer of magnetized ferromagnetic powder particles displacing at least a portion of said organic layer, wherein said ferromagnetic particles are held in the depressions in said organic layer in image-wise configuration and said ferromagnetic particles have a diameter along at least one axis, of at least 0.3 micron but less than 25 times the thickness of said organic layer.

Broadly speaking, the present method of depositing ferromagnetic powders differs from known methods of depositing powders in various subtle and unobvious ways. For example, the ferromagnetic particles that form the image are not merely dusted on, but instead are applied against the surface of the light-sensitive organic layer under moderate physical force after exposing the light-sensitive layer to actinic radiation. The relatively soft or particle-receptive nature of the light-sensitive layer is such that substantially a monolayer of particles or isolated small agglomerates of a predetermined size, are at least partially embedded at the surface of the light-sensitive layer by moderate physical force. The surface condition in the particle receptive area is at most only slightly soft but not fluid as in prior processes. The relatively hard or particle non-receptive condition of the light-sensitive surface in the non-image areas is such that when powder particles of a predetermined size are applied under the same moderate physical force few, if any, are embedded sufficiently to resist removal by moderate dislodging action such as blowing air against the surface. Any particles remaining in the non-image areas are removed readily by rubbing a soft pad over the surface.

For use in this invention, the solid, light-sensitive organic layer, which can be an organic material in its naturally occurring or manufactured form or a mixture of said organic material with plasticizers and/or photoactivators for adjusting the powder receptivity and sensitivity to actinic radiation, must be capable of developing a predetermined contrast or  $R_d$  using a suitable black developing powder under the

conditions of development. The powder-receptive areas of the layer (unexposed areas of a positive-acting, light-sensitive layer or the exposed areas of a negative-acting material) must have a softness such that suitable particles can be embedded into a stratum at the surface of the light-sensitive layer by mild physical forces. However, the layer should be sufficiently hard that film transparencies can be pressed against the surface without the surfaces sticking together or being damaged even when heated slightly under high intensity light radiation. The light-sensitive layer should also have a degree of toughness so that it maintains its integrity during development. If the  $R_d$  of the light-sensitive layer is below about 0.2, the light-sensitive layer is too hard to accept a suitable concentration of particles. On the other hand, if the  $R_d$  is above about 2.2 the light-sensitive layer is so soft that it is difficult to maintain film integrity during physical development. Further, if the  $R_d$  is above 2.2, the light-sensitive layer is so soft that the layer may be displaced by mechanical forces resulting in distortion or destruction of the image. Accordingly, for use in this invention the light-sensitive layer must be capable of developing a  $R_d$  within the range of 0.2 to 2.2, or preferably 0.4 to 2.0 using a suitable black developing powder under the conditions of development.

The  $R_d$  of the positive-acting, light-sensitive layer, which can be called  $R_{dp}$ , is a photometric measurement of the reflection density of a black powder developed light-sensitive layer after a positive-acting, light-sensitive layer has been exposed to sufficient actinic radiation to convert the exposed areas into a substantially powder-non-receptive state (clear the background). The  $R_d$  of a negative-acting, light-sensitive layer, which is called  $R_{dn}$ , is a photometric measurement of the reflection density of a black powder developed area, after a negative-acting, light-sensitive layer has been exposed to sufficient radiation to convert the exposed area into a powder-receptive area.

In somewhat greater detail, the reflection density of the solid positive-acting, light-sensitive layer ( $R_{dp}$ ) is determined by coating the light-sensitive layer on a white substrate, exposing the light-sensitive layer to sufficient actinic radiation image-wise to clear the background of the solid, positive-acting, light-sensitive layer, applying a black powder (prepared from 77% pliolite VTL (the word "Pliolite" is a Registered Trade Mark) and 23% Neo Spectra carbon black in the manner described below) to the exposed layer, physically embedding said black powder under the conditions of development as a monolayer in a stratum at

the surface of said light-sensitive layer and removing the non-embedded particles from said light - sensitive layer. The developed organic layer containing black powder embedded image areas and substantially powder free non-image areas is placed in a standard photometer having a scale reading from 0 to 100% reflection of incident light or an equivalent density scale, such as on Model 500A photometer of the Photovolt Corporation. The instrument is zeroed (0 density; 100% reflectance) on a powder free non-image area of the light-sensitive organic layer and an average  $R_d$  reading is determined from the powder developed area. The reflection density is a measure of the degree of blackness of the developed surface which is relatable to the concentration of particles per unit area. The reflection density of a solid, negative-acting light-sensitive layer ( $R_{dn}$ ) is determined in the same manner except that the negative-acting light-sensitive layer is exposed to sufficient actinic radiation to convert the exposed area into a powder-receptive state. If the  $R_d$  under the conditions of development is between 0.2 (63.1% reflectance) and 2.2 (0.63% reflectance), or preferably between 0.4 (39.8% reflectance) and 2.0 (1.0% reflectance), the solid, light-sensitive organic material deposited in a layer is suitable for use in this invention.

Although the  $R_d$  of all light-sensitive layers is determined by using the aforesaid black developing powder and a white substrate, the  $R_d$  is only a measure of the suitability of a light-sensitive layer for use in this invention.

Since the  $R_d$  of any light-sensitive layer is dependent on numerous factors other than the chemical constitution of the light-sensitive layer, the light-sensitive layer is best defined in terms of its  $R_d$  under the development conditions of intended use. The positive-acting, solid, light-sensitive organic layers useful in this invention must be powder receptive in the sense that the aforesaid black developing powder can be embedded as a monoparticle layer into a stratum at the surface of the unexposed layer to yield a  $R_{dp}$  of 0.2 to 2.2 (0.4 to 2.0 preferably) under the predetermined conditions of development and light-sensitive in the sense that upon exposure to actinic radiation the most exposed areas can be converted into the non-particle receptive state (background cleared) under the predetermined conditions of development. In other words, the positive-acting, light-sensitive layer must contain a certain inherent powder receptivity and light-sensitivity. The positive-acting, light-sensitive layers are apparently converted into the powder-non-receptive state by a light-

catalyzed hardening action, such as photopolymerization, photocrosslinking or photooxidation. Some of these photohardening reactions are dependent on the presence of oxygen, such as the photooxidation of internally ethylenically unsaturated acids and esters while others are inhibited by the presence of oxygen, such as those based on the photopolymerization of the vinylidene groups of polyvinylidene monomers alone or together with polymeric materials. The latter require special precautions, such as storage in oxygen-free atmosphere or oxygen-impermeable cover sheets. For this reason, it is preferable to use solid, positive-acting, film-forming, organic materials containing no terminal ethylenic unsaturation.

The negative-acting, solid light-sensitive organic layers useful in this invention must be light-sensitive in the sense that, upon exposure to actinic radiation, the most exposed areas of the light-sensitive layer are converted from a non-powder-receptive state under the predetermined conditions of development to a powder-receptive state under the predetermined conditions of development. In other words, the negative-acting, light-sensitive layer must have a certain minimum light-sensitivity and potential powder receptivity. The negative-acting, light-sensitive layers are apparently converted into the powder receptive state by a light-catalyzed softening action, such as photodepolymerization.

In general, the positive-acting, solid, light-sensitive layers useful in this invention comprise a film-forming organic material in its naturally occurring or manufactured form or a mixture of said organic material with plasticizers and/or photoactivators for adjusting powder receptivity and sensitivity to actinic radiation. Suitable positive - acting, film - forming organic materials which are not inhibited by oxygen, include internally ethylenically unsaturated acids, such as abietic acid, rosin acids, partially hydrogenated rosin acids, such as those sold under the name Staybelite resin, wood rosin, esters of internally ethylenically unsaturated acids, methylol amides of maleated oils such as described in U.S. Patent 3,471,466, phosphatides of the class described in U.S. Patent No. 3,585,031, such as soybean lecithin, partially hydrogenated lecithin, dilinolenyl alpha-lecithin, partially hydrogenated rosin acid esters, such as those sold under the name Staybelite esters, rosin modified alkyds; polymers of ethylenically unsaturated monomers, such as vinyltoluene-alpha methyl styrene copolymers, polyvinyl cinamate, polyethyl methacrylate, vinyl acetate-vinyl stearate copolymers, polyvinyl pyrrolidone; coal tar resins, such as coumarone - indene resins, halogenated

hydrocarbons, such as chlorinated waxes, chlorinated polyethylene. Positive - acting, light-sensitive materials, which are inhibited by oxygen include mixtures of polymers, such as polyethylene terephthalate/sebacate, or cellulose acetate or acetate/butyrate, with polyunsaturated vinylidene monomers, such as ethylene glycol diacrylate or dimethacrylate, tatraethylene glycol diacrylate or dimethacrylate.

Although numerous positive-acting, film-forming organic materials have the requisite light-sensitivity and powder-receptivity at predetermined development temperatures, it is generally preferable to compound the film-forming organic material with photoactivator(s) and/or plasticizer(s) to impart optimum powder-receptivity and light-sensitivity to the light-sensitive layer. In most cases, the light-sensitivity of an element can be increased many fold by incorporation of a suitable photoactivator capable of producing free-radicals, which catalyze the light-sensitive reaction and reduce the amount of photons necessary to yield the desired physical change.

Suitable photoactivators capable of producing free-radicals include benzil, benzoin, Michlers ketone, diacetyl, phenanthraquinone, p-dimethylaminobenzoin, 7, 8-benzoflavone, trinitrofluorenone, desoxybenzoin, 2,3-pentanedione, dibenzylketone, nitroisatin, di(6-dimethylamino-3-pyridyl)methane, metal naphthanates, N-methyl-N-phenylbenzylamine, pyridil, 5-7 dichloroisatin, azodiisobutyronitrile, trinitroanisole, chlorophyll, isatin, and bromoisatin. These compounds can be used in a concentration of .001 to 2 times the weight of the film-forming organic material (.1%-200% the weight of the film former). As in most catalytic systems, the best photoactivator and optimum concentration thereof is dependent upon the film-forming organic material. Some photoactivators respond better with one type of film former and may be useful over rather narrow concentration ranges whereas others are useful with substantially all film formers in wide concentration ranges.

The acyloin and vicinal diketone photoactivators, particularly benzil and benzoin are preferred. Benzoin and benzil are effective over wide concentration ranges with substantially all film-forming light-sensitive organic materials. Benzoin and benzil have the additional advantage that they have a plasticizing or softening effect on film-forming light-sensitive layers, thereby increasing the powder-receptivity of the light-sensitive layers. When employed as a photoactivator, benzil should preferably comprise at least 1% by weight of the film-forming organic material (.01 times the film former weight).

Dyes, optical brighteners and light ab-

sorbers can be used alone or preferably in conjunction with the aforesaid free-radical producing photoactivators (primary photoactivators) to increase the light-sensitivity of the light-sensitive layers of this invention by converting light rays into light rays of longer lengths. For convenience, these secondary photoactivators (dyes, optical brighteners and light absorbers) are called "superphotoactivators". Suitable dyes, optical brighteners and light absorbers include 4-methyl-7-dimethylaminocoumarin, Calcofluor yellow HEB (preparation described in U.S. Patent 2,415,373), Calcofluor white SB super 30080, Calcofluor, Uvitex W conc. (the word "Uvitex" is a Registered Trade Mark), Uvitex TXS conc., Uvitex RS (described in Textil-Rundschau 8 [1953], 339), Uvitex WGS conc., Uvitex K, Uvitex CF conc., Uvitex W (described in Textil-Rundschau 8, [1953], 340), Aclarat 8678, Blancophor OS (the word "Blancophor" is a Registered Trade Mark), Tenopol UNPL, MDAC S-8844, Uvinul 400 (the word "Uvinul" is a Registered Trade Mark), Thilflavin TGN conc., Aniline yellow - S (low conc.), Seto flavine T 5506-140 (the word "Seto" is a Registered Trade Mark), Auramine O, Calozine yellow OX, Calcofluor RW, Calcofluor GAC, Acetosol yellow 2 RLS-PHF, Eosine bluish, Chinoline yellow - P conc., Ceniline yellow S (high conc.), Anthracene blue Violet fluorescence, Calcofluor white MR, Tenopol PCR, Uvitex GS, Acid-yellow-T supra, Acetosol yellow 5 GLS, Calcocid OR, Y, Ex. Conc., diphenyl brilliant flavine 7 GFF, Resoflorm fluorescent yellow 3 CPI, Eosin yellowish, Thiazole fluorescor, G, Pyrazalone organe YB-3, and National FDeC yellow. Individual superphotoactivators may respond better with one type of light-sensitive organic film-former and photoactivator than with others. Further, some photoactivators function better with certain classes of brighteners, dyes and light absorbers. For the most part, the most advantageous combinations of these materials and proportions can be determined by simple experimentation.

As indicated above, plasticizers can be used to impart optimum powder receptivity to the light-sensitive layer. With the exception of lecithin, most of the film-forming, light-sensitive organic materials useful in this invention are not powder-receptive at room temperature but are powder-receptive above room temperature. Accordingly, it is desirable to add sufficient plasticizer to impart room temperature (15 to 30°C.) or ambient temperature powder receptivity to the light-sensitive layers and/or broaden the  $R_{40}$  range of the light-sensitive layers.

While various softening agents, such as dimethyl siloxanes, dimethyl phthalate, gly-

cerol or vegetable oils, can be used as plasticizers, benzil and benzoin are preferred since, as pointed out above, these materials have the additional advantage that they increase the light-sensitivity of the film-forming organic materials. As plasticizer-photoactivators, benzoin and benzil are preferably used in a concentration of 1% to 80% by weight of the film-forming solid organic material.

The preferred positive-acting, light-sensitive film formers containing no conjugated terminal ethylenic unsaturation include the esters and acids of internally ethylenically unsaturated acids, particularly the phosphatides, rosin acids, partially hydrogenated rosin acids and the partially hydrogenated rosin esters. These materials, when compounded with suitable photoactivators, preferably acyloins or vicinal diketones together with superphotoactivators require less than 2 minutes exposure to clear the background of light-sensitive layers and can be developed to yield ferromagnetic powder patterns having the desired configuration.

In general, the negative-acting, light-sensitive layers useful in this invention comprise a film-forming organic material in its naturally occurring or manufactured form, or a mixture of said organic material with plasticizers and/or photoactivators for adjusting powder receptivity and sensitivity to actinic radiation. Suitable negative-acting, film-forming organic materials include n-benzyl linoleamide, dilinoleyl-alpha-lecithin, castor wax (glycerol 12-hydroxy-stearate), ethylene glycol monohydroxy stearate, polyisobutylene and polyvinyl stearate. Of these, castor wax and other hydrogenated ricinoleic acid esters (hydroxystearate) are preferred. These materials can be compounded with plasticizers and/or photoactivators in the same manner as the positive-acting, light-sensitive film-forming organic materials.

In somewhat greater detail, magnetic patterns are produced by applying a thin layer of solid, light-sensitive, film-forming organic material having a potential  $R_d$  of 0.2 to 2.2 (i.e. capable of developing a  $R_d$  or  $R_m$  of 0.2 to 2.2) to a non-magnetic base by any suitable means dictated by the nature of the film-forming organic material and/or the base (e.g. hot-melt, draw down, spray, roller coating or air knife, flow, dip or curtain coating) so as to produce a reasonably smooth homogeneous layer of from 0.1 to 40 microns thick employing suitable solvents, as necessary. Suitable bases for use in this invention comprise transparent or opaque film bases composed of one or more flexible layers. Suitable layers include cellulose esters (e.g. cellulose acetate, cellulose propionate, or cellulose butyrate), polyesters (polyethylene tereph-

thalate), nylon, polystyrene, polypropylene, or corona discharge polypropylene. In general, the base employed should have relatively good dimensional stability in the sense that it does not stretch when wound up under tension.

The light-sensitive layer must be at least 0.1 micron thick, and preferably at least 0.4 micron, in order to hold ferromagnetic powders during development. If the light-sensitive layer is less than 0.1 micron, or the powder diameter is more than 25 times layer thickness, the light-sensitive layer does not hold the powder with the necessary tenacity. In general, as layer thickness increases, the light-sensitive layer is capable of holding larger particles. However, as the light-sensitive layer thickness increases, it becomes increasingly difficult to maintain film integrity during development. Accordingly, the light-sensitive layer must be from 0.1 to 40 microns, preferably from 0.4 to 10 microns.

The light-sensitive layers of predetermined thickness are preferably applied to the base from an organic solvent (hydrocarbon, such as hexane, heptane or benzene; halogenated hydrocarbon, such as chloroform, carbon tetrachloride, 1,1,1-trichloroethane, or trichloroethylene. If desired, the light-sensitive layers can be deposited from suitable aqueous emulsions. The thickness of the light-sensitive layer can be varied as a function of the concentration of the solids dissolved in the solvent.

After the base is coated with a suitable solid, light-sensitive organic layer, a latent image is formed by exposing the element to actinic radiation in image-receiving manner in predetermined areas corresponding to an optical pattern for a time sufficient to provide a potential  $R_d$  of 0.2 to 2.2. The light-sensitive elements can be exposed to actinic light through a suitable optical master of the sound track or information to be reproduced. If desired, a magnetic reader may be employed to obtain an optical master from a magnetic tape or disc. In general, optimum speed is attained when a preformed optical master is employed.

As indicated above, the latent images are preferably produced from positive-acting, light-sensitive layers by exposing the element in image-receiving manner for a time sufficient to clear the background, i.e. render the exposed areas non-powder-receptive. As explained in commonly assigned British Patent No. 1,296,709 the amount of actinic radiation necessary to clear the background varies to some extent with developer size and development conditions. Due to these variations it is often desirable to slightly overexpose both positive and negative-acting, light-sensitive elements.

After the light-sensitive element is exposed to actinic radiation for a time sufficient to clear the background of the positive-acting, light-sensitive layer or establish a potential  $R_{an}$  of 0.2 to 2.2, a ferromagnetic powder is applied to the light-sensitive layer. The ferromagnetic powder, which has a diameter or dimension along one axis of at least 0.3 micron, is applied physically with a suitable force, preferably mechanically, to embed the powder in the light-sensitive layer. The developing powder can be virtually any shape, such as spherical, acicular or platelets, provided it has a diameter along at least one axis of at least 0.3 micron.

The ferromagnetic powders, include iron powders, (iron oxides), nickel alloys and cobalt alloys. These powders can be applied in a substantially pure form or on a suitable carrier. Carriers, such as resinous or polymeric materials, can be employed to regulate the particle size of the ferromagnetic powders or, as explained below, to improve the wear resistance of the ferromagnetic tapes. The ferromagnetic powders can be ball-milled with polymeric carrier in order to coat the carrier with active ingredient, or, if desired, they can be blended above the melting point of resinous carrier, ground to suitable size and classified.

The black developing powder for determining the  $R_a$  of a light-sensitive layer, which can also be employed as a suitable light-absorbing pigment in this invention is formed by heating about 77% Pliolite VTL (vinyltoluene-butadiene copolymer) and 23% Neo Spectra carbon black at a temperature above the melting point of the resinous carrier, blending on a rubber mill for fifteen minutes and then grinding in a Mikro-atomizer.

The developing powders useful in this invention contain particles having a diameter or dimension along at least one axis from 0.3 to 40 microns, preferably from 0.5 to 10 microns, with powders of the order of 1 to 15 microns being best for light-sensitive layers of 0.4 to 10 microns. Maximum particle size is dependent on the thickness of light-sensitive layer while minimum particle size is independent of layer thickness. Electron microscope studies have shown that powders having a diameter 25 times the thickness of the light-sensitive layer cannot be permanently embedded into light-sensitive layers, and generally speaking, best results are obtained where the diameter of the powder particle is less than about 10 times the thickness of the light-sensitive layer. For the most part, particles over 40 microns are not detrimental to image development provided the developing powder contains a reasonable concentration

of powder particles under 40 microns, which are less than 25 times, and preferably less than 10 times, the light-sensitive layer thickness.

Although developing powders over 40 microns are not detrimental to image development, the presence of particles under 0.3 micron diameter along all axes can be detrimental. In general, it is preferable to employ developing powders having substantially all powders having a diameter along at least one axis not less than 0.3 micron, preferably more than 0.5 micron, since particles less than 0.3 micron tend to embed in non-image areas. As the particle size of the smallest powder in the developer increases, less exposure to actinic radiation is required to clear the background.

For best results, the developing powder should have substantially all particles (at least 95% by weight) over 1 micron in diameter along one axis and preferably from 1 to 15 microns for use with light-sensitive layers of from 0.4 to 10 microns. In this way, powder embedment in image areas is maximum.

In somewhat greater detail, the developing powder is applied directly to the light-sensitive layer, while the powder receptive areas of said layer are in at most only a slightly soft condition and said layer is at a temperature below the melting point of the layer and powder. The powder is distributed over the area to be developed and physically embedded into the stratum at the surface of the light-sensitive layer, preferably mechanically by force having a lateral component, such as to-and-fro and/or circular rubbing or scrubbing action using a soft pad or fine brush. If desired, the powder may be applied separately or contained in the pad or brush. The quantity of powder is not critical provided there is an excess available beyond that required for full development of the area, as the development seems to depend primarily on particle - to - particle interaction rather than brush - to - surface or pad - to - surface forces to embed a layer of powder particles substantially one particle thick (monoparticle layer) into a stratum at the surface of the light-sensitive layer. Only a single stratum of powder particles penetrates into the powder-receptive areas of the light-sensitive layer even if the light-sensitive layer is several times thicker than the developer particle diameter.

The pad or brush used for development is critical only to the extent that it should not be so stiff as to scratch or scar the film surface when used with moderate pressure with the preferred amount of powder to develop the film. Ordinary absorbent cotton loosely compressed into a pad about

the size of a baseball and weighing about 3 to 6 grams is especially suitable. The developing motion and force applied to the pad during development is not critical. The speed of the swabbing action is not critical other than that it affects the time required; rapid movement requiring less time than slow. The preferred mechanical action involved is essentially the lateral action applied in ultrafine finishing of a wood surface by hand sanding or steel wooling.

Hand swabbing is entirely satisfactory, and when performed under the conditions described above, will reproducibly produce the maximum density which the material is capable of achieving. That is, the maximum concentration of particles per unit area will be deposited under the prescribed conditions, dependent upon the physical properties of the material such as softness, resiliency, plasticity, and cohesivity. Substantially the same results can be achieved using a mechanical device for the powder application. A rotating or rotating and oscillating, cylindrical brush or pad may be used to provide the described brushing action and will produce a substantially similar end result.

After the application of developing powder, excess powder remains on the surface which has not been sufficiently embedded into, or attached to, the base. This may be removed in any convenient way, as by wiping with a clean pad or brush usually using somewhat more force than employed in mechanical development, by vacuuming, by vibrating, by air doctoring or by air jets, and recovered. For simplicity and uniformity of results, the excess powder usually is blown off using an air gun having an air line pressure of about 20 to 40 psi. The gun is preferably held at an angle of about 30 to 60 degrees to the surface at a distance of 1 to 12 inches (3 to 8 preferred). The pressure at which the air impinges on the surface is about 0.1 to 3, and preferably about 0.25 to 2, pounds per square inch. Air cleaning may be applied for several seconds or more until no additional loosely held particles are removed. The remaining powder should be sufficiently adherent to resist removal by moderately forceful wiping or other reasonably abrasive action.

The resultant ferromagnetic imaged tape is then activated by passing the tape through a suitable magnetic field, such as a 3-kilogauss field. In some cases it may be advantageous to use an alternating magnetic field to superimpose a second frequency on the magnetic pattern.

Either before or after activation of the magnetic tape, it can be sprayed with a thin clear polymeric layer, such as an acrylic lacquer to provide sufficient wear re-

sistance or to permit repeated operation in typical play-back equipment. Alternatively, where the ferromagnetic developing powder is on a resinous or polymeric carrier, additional wear resistance can be attained by fusing the carrier to the base with heat or solvent vapors for the carrier.

In the event that the sound or informational track of tapes produced in this manner is erased or wiped out, the sound or informational track is not lost but can be reinstated by merely passing the tape through a suitable magnetic field.

The following examples are merely illustrative and should not be construed as limiting the scope of this invention.

#### EXAMPLE 1

A Mylar (the word "Mylar" is used as a Registered Trade Mark for polyethylene terephthalate) film was flow coated with a solution comprising .96 grams Staybelite Ester #10 (partially hydrogenated rosin ester of glycerol), .24 grams benzil and .144 grams 4-methyl-7-dimethylaminocoumarin, dissolved in 100 mls. Chloroethane (1,1,1-trichloroethane) to form a one micron light-sensitive layer. The sensitized side of the element was placed in contact with an optical informational line master and exposed to actinic radiation in a vacuum frame for about one minute. The unexposed areas were developed with magnetic recording ferric oxide IRN-110. The iron oxide was embedded into the unexposed areas of the light-sensitive Staybelite layer by rubbing a wad of cotton over the surface of the element using essentially the same force as employed in the ultrafine finishing of wood resolving 120 line pairs per mm. The non-embedded iron oxide was removed from the surface of the light-sensitive element. The tape was spray coated with a thin, clear acrylic lacquer. After the acrylic lacquer dried, the tape was activated by pulling it through a 3-kilogauss field at a speed exceeding 120" per second.

A full gain output of 1.1 volts was developed at the output of a tape recorder for the reproduced magnetic tape. An oscilloscope analysis of a 40-bit reproducibility sampling showed that the "0" bit had a mean of  $16 \pm 16\%$  and a "1" bit of  $84 \pm 16\%$ . At a playback speed of 3-3/4 ips, an edge rise time of 59% per 0.001" was measured. The storage density of the tape was about 1500 bits per inch.

Essentially the same results are obtained by replacing the Staybelite ester composition described above with an optical master of a sound track and (1) 1.25 grams Staybelite Ester #5 (partially hydrogenated rosin ester of glycerol), 1.875 grams



- benzil and .3125 grams 4-methyl-7-dimethylaminocoumarin, dissolved in 100 mls. Chlorothene, (2) 1.25 grams Staybelite Rosin F (partially hydrogenated rosin acids), .1 gram benzil and .3125 grams 4-methyl-7-dimethylaminocoumarin, dissolved in 100 mls. Chlorothene, (3) 1.25 grams wood rosin, .15 grams benzil and .3125 grams 4-methyl-7-diethylaminocoumarin, dissolved in 100 mls. Chlorothene, and (4) 1.25 grams abietic acid, .15 grams benzil and .3125 grams 4-methyl-7-dimethylaminocoumarin dissolved in 100 mls. Chlorothene.

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**EXAMPLE II**

- The magnetic tape reproduced in Example I was wiped out using a magnetic field and then reestablished by passing the tape through a second 3-kilogauss magnetic field completely reproducing the original informational track.

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**EXAMPLE III**

- Essentially the same results are obtained when Example I is repeated using iron developing powder in place of ferric oxide.

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**EXAMPLE IV**

- Essentially the same results are obtained when Example I is repeated using a continuous tone master in place of the line master.

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**WHAT WE CLAIM IS:**

1. An article with a surface having a permanent magnetic pattern comprising a non-magnetic base bearing a solid organic layer of 0.1 to 40 microns thickness, said organic layer comprising the product of an exposed photo-sensitive organic material and containing a mono-layer of magnetized ferromagnetic powder particles displacing at least a portion of said organic layer, wherein said ferromagnetic particles are held in the depressions in said organic layer in image-wise configuration and said ferromagnetic particles have a diameter, along at least one axis, of at least 0.3 micron but less than 25 times the thickness of said organic layer.

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(2) A process for the production of an article with a surface having a permanent magnetic pattern as claimed in claim 1 which comprises exposing a non-magnetic base bearing a solid, light-sensitive organic layer of 0.1 to 40 microns thickness and capable of developing a  $R_d$  of 0.2 to 2.2 to actinic radiation in predetermined areas corresponding to an optical pattern to establish a potential  $R_d$  of 0.2 to 2.2; applying to the layer of organic material, free-flowing ferromagnetic powder particles, the free-flowing powder having a diameter, along at least one axis of at least 0.3 micron but less than 25 times the thickness of the organic layer; while the layer is at a temperature below the melting point of the organic layer, physically embedding the ferromagnetic particles as a monolayer in a stratum at the surface of the light-sensitive layer to yield an image having portions varying in density in proportion to the exposure of each portion; removing non-embedded particles from the organic layer to develop a discrete permanent pattern of ferromagnetic material and magnetizing the resultant ferromagnetic material to establish a magnetic pattern corresponding to the original optical pattern.

3. A process as claimed in claim 2 wherein the base is a substantially dimensionally stable film.

(4) A process as claimed in claim 2 or 3 wherein the ferromagnetic imaged film is lacquered.

5. A process as claimed in any of claims 2 to 4 wherein the ferromagnetic powder comprises a polymeric or resinous carrier and said carrier is fused after development.

6. A process as claimed in claim 4 or 5 wherein the light-sensitive layer is capable of developing a  $R_d$  of 0.4 to 2.2.

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